

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|--|--|
| (51) International Patent Classification 6 : C08F 210/18, 297/08, 2/00, 2/14 | A1 | (11) International Publication Number: WO 98/02471 (43) International Publication Date: 22 January 1998 (22.01.98) |
| (21) International Application Number: PCT/US97/12294 (22) International Filing Date: 9 July 1997 (09.07.97) (30) Priority Data: 08/679,538 12 July 1996 (12.07.96) US (60) Parent Application or Grant (63) Related by Continuation US 08/679,538 (CIP) Filed on 12 July 1996 (12.07.96) (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY (US/US); 2030 Dow Center, Mid- land, MI 48674 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): KOLTHAMMER, Brian, W., S. [CA/US]; 109 Rosewood, Lake Jackson, TX 77566 (US). CARDWELL, Robert, S. [US/US]; 106 Any Way, Lake Jackson, TX 77566 (US). PARIKH, Deepak [US/US]; 59 North Trillium Court, Lake Jackson, TX 77566 (US). EDMONDSON, Morris, S. [US/US]; 130 Mohawk Drive, Route 7, Alvin, TX 77511 (US). SMITH, Stanley, W. [US/US]; 124 Tulip Trail, Lake Jackson, TX 77566 (US). | (74) Agent: WARRICK, Noreen, D.; Patent Dept., B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> | |
| (54) Title: ELASTOMERS AND PROCESS FOR THEIR MANUFACTURE (57) Abstract A process for polymerizing ethylene, α -olefin and optionally diene monomers is disclosed. The process comprises the steps of contacting: (1) ethylene, (2) at least one C ₃ -C ₂₀ aliphatic α -olefin, (3) optionally, at least one C ₄ -C ₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) an activator, and (5) a solvent. The process can be conducted in a single or multiple reactors, and if in multiple reactors, then the reactors can be configured in series or parallel. Solvent is removed from the polymer stream in an anhydrous, first stage solvent recovery operation such that the solids concentration of the product stream is increased by at least 100 percent. Additional solvent is removed in an anhydrous, second stage solvent recovery operation from the product of the first stage solvent recovery operation such that the solids concentration of the product stream is in excess of 65 weight percent. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | | TR | Turkey |
| BG | Bulgaria | HU | Hungary | ML | Mali | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MN | Mongolia | UA | Ukraine |
| BR | Brazil | IL | Israel | MR | Mauritania | UG | Uganda |
| BY | Belarus | IS | Iceland | MW | Malawi | US | United States of America |
| CA | Canada | IT | Italy | MX | Mexico | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NE | Niger | VN | Viet Nam |
| CG | Congo | KE | Kenya | NL | Netherlands | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NO | Norway | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | NZ | New Zealand | | |
| CM | Cameroon | KR | Republic of Korea | PL | Poland | | |
| CN | China | KZ | Kazakhstan | PT | Portugal | | |
| CU | Cuba | LC | Saint Lucia | RO | Romania | | |
| CZ | Czech Republic | LJ | Liechtenstein | RU | Russian Federation | | |
| DE | Germany | LK | Sri Lanka | SD | Sudan | | |
| DK | Denmark | LR | Liberia | SE | Sweden | | |
| EE | Estonia | | | SG | Singapore | | |

ELASTOMERS AND PROCESS FOR THEIR MANUFACTURE

This invention relates to elastomers. In one aspect, this invention relates to ethylene-propylene (EP) and ethylene-propylenediene monomer (EPDM) elastomers while in another aspect, this invention relates to a process for their manufacture. In yet another aspect, this invention relates to elastomers made by a process in which the catalyst is a metallocene complex, more particularly to a class of Group 4 metal complexes.

Metallocene complexes and methods for their preparation are disclosed in US-A-5,470,993 (published also as EP-A-705,269 and WO95/00526); USSN 545,403, filed July 3, 1990 (published also as EP-A-416,815); USSN 547,718, filed July 3, 1990 (published also as EP-A-468,651); USSN 702,475, filed May 20, 1991 (published also as EP-A-514,828); USSN 876,268, filed May 1, 1992, (published also as EP-A-520,732) and USSN 8,003, filed January 21, 1993 (published also as WO93/19104), as well as US-A-5,055,438, US-A-5,057,475, US-A-5,096,867, US-A-5,064,802, US-A-5,132,380.

The term "elastomer" was first defined in 1940 to mean synthetic thermosetting high polymers having properties similar to those of vulcanized natural rubber, that is, having the ability to be stretched to at least twice their original length and to retract very rapidly to approximately their original length when released. Representative of these "high polymers" were styrene-butadiene copolymer, polychloroprene, nitrite butyl rubber and ethylene-propylene terpolymers (also known as EPDM rubbers). The term "elastomer" was later extended to include uncrosslinked thermoplastic polyolefins, TPO's.

ASTM D 1566 defines various physical properties, and the test methods for measuring these properties, of rubbers. USP 5,001,205 (Hoel) provides an overview of the known elastomers comprising ethylene copolymerized with an α -olefin. As Hoel describes, commercially viable elastomers have various minimum properties, such as a Mooney viscosity no less than 10, a weight average molecular weight (Mw) no less than 110,000, a glass transition temperature below -40°C , and a degree of crystallinity no greater than 25 percent. USP 5,001,205 discloses a process for polymerizing high molecular weight elastomers using liquid phase polymerization in the presence of a metallocene/alumoxane (specifically, a bis(cyclopentadienyl) alumoxane) catalyst.

We have now discovered a process for the manufacture of ethylenepropylene and ethylene/ α -olefin/diene monomer polymers. In one embodiment, the process is characterized by the following steps:

- A. contacting in a first reactor (1) ethylene, (2) at least one C_3 - C_{20} aliphatic α -olefin, (3) optionally, at least one C_4 - C_{20} diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent, the first reactor operated such that a first product is produced at a solids concentration

of from 1 to 15 weight percent, based on the weight of the reaction mass in the first reactor;

- 5 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, (5) a solvent, and (6) a product stream from the first reactor, the second reactor operated such that a second product is produced at a solids concentration of from 2 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- 10 C. removing a product stream from the second reactor;
- D. removing solvent from the product stream of the second reactor in an anhydrous, first stage solvent recovery operation such that the solids concentration of the product stream is increased by at least 100 percent; and
- 15 E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the product of first stage solvent recovery operation such that the solids concentration of the product stream is in excess of 65 weight percent.

In another embodiment of this invention, the process is characterized by additional anhydrous solvent recovery operations in which the solids concentration of the final product is increased to greater than 99 weight percent. Preferably, the product of the first reactor has a weight average molecular weight greater than that of the product of the second reactor.

20 In yet another embodiment, the process is characterized by the following steps:

- 25 A. contacting in a first reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent, the first reactor operated such that a first product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the first reactor;
- 30 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, (b) at least one activator, and (5) a solvent, the second reactor operated such that a second product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- C. recovering a product stream from each of the first and second reactors, and then blending these individual product streams into a combined product stream;

D. removing solvent from the combined product stream in an anhydrous, first stage solvent recovery operation such that the solids concentration of the combined product stream is increased by at least 100 percent; and

E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the combined product stream such that the solids concentration of the combined product stream is in excess of 65 weight percent.

In another embodiment of this invention, the process is further characterized by additional anhydrous solvent recovery operations in which the solids concentration of the final product is increased to greater than 99 weight percent. Preferably, the product of one reactor has a weight average molecular weight greater than that of the product of the other reactor.

Figure 1 is a diagrammatic representation of the two principal zones of the polymerization process of this invention.

Figure 2 is a diagrammatic representation of a single reactor embodiment of Zone I of Figure 1.

Figure 3 is a diagrammatic representation of an in-series dual reactor configuration of Zone I of Figure 1.

Figure 4 is a diagrammatic representation of an in-parallel dual reactor configuration of Zone I of Figure 1.

Figure 5 is a diagrammatic representation of four possible three-reactor configurations of Zone I of Figure 1.

Figure 6 is a diagrammatic representation of one embodiment of Zone II of Figure 1.

The elastomers made according to the new process disclosed herein are interpolymers of ethylene ($\text{CH}_2=\text{CH}_2$) with at least one comonomer selected from the group consisting of aliphatic C_3 - C_{20} α -olefins, conjugated dienes, and nonconjugated dienes. The term interpolymers includes copolymers, such as ethylene propylene (EP) copolymers, and terpolymers, such as EPDM, but is not intended to limit the elastomers made to only one or two monomers copolymerized with ethylene. Examples of the aliphatic C_3 - C_{20} α -olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. The α -olefin can also contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an α -olefin such as 3-cyclohexyl-1-propene (allylcyclohexane) and vinyl-cyclohexane. Although not α -olefins in the classical sense of the term, certain cyclical olefins such as norbornene and related olefins can be used in place of some or all of the α -olefins.

Examples of nonconjugated dienes include aliphatic dienes such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, 1,6-heptadiene, 6-methyl-1,5-heptadiene, 1,6-octadiene, 1,7-octadiene, 7-methyl-1,6-octadiene, 1,13-tetradecadiene, and 1,19-eicosadiene; cyclic dienes such as

1,4-cyclohexadiene, bicyclo[2.2.1]hept-2,5-diene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, bicyclo[2.2.2]oct-2,5-diene, 4-vinylcyclohex-1-ene, bicyclo[2.2.2]oct-2,6-diene, 1,7,7-trimethylbicyclo-[2.2.1]hept-2,5-diene, dicyclopentadiene, methyltetrahydroindene, 5-allylbicyclo[2.2.1]hept-2-ene, and 1,5-cyclooctadiene; aromatic dienes such as 1,4-diallylbenzene, 4-allyl-1H-indene; and trienes such as 2,3-diisopropenyldiene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene, 2-propenyl-2,5-norbornadiene, 1,3,7-octatriene, and 1,4,9-decatriene; with 5-ethylidene-2-norbornene being a preferred nonconjugated diene.

Examples of conjugated dienes include butadiene, isoprene, 2,3-dimethylbutadiene-1,3, 1,2-dimethylbutadiene-1,3, 1,4-dimethylbutadiene-1,3, 1-ethylbutadiene-1,3, 2-phenylbutadiene-1,3, hexadiene-1,3, 4-methylpentadiene-1,3, 1,3-pentadiene ($\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$; commonly called piperylene), 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 3-ethyl-1,3-pentadiene; with 1,3-pentadiene being a preferred conjugated diene.

Copolymers of ethylene and one aliphatic $\text{C}_3\text{-C}_{20}$ α -olefin or one diene (either conjugated or nonconjugated) can be prepared using the process of this invention. Interpolymers of ethylene, at least one aliphatic $\text{C}_3\text{-C}_{20}$ α -olefin, and/or at least one diene (either conjugated or nonconjugated) can also be made by using this process. Exemplary copolymers include ethylene/propylene and ethylene/1-octene. Exemplary terpolymers include ethylene/propylene/1-octene, ethylene/propylene/5-ethylidene-2-norbornene, ethylene/1-octene/5-ethylidene-2-norbornene, ethylene/propylene/1,3-pentadiene, and ethylene/1-octene/1,3-pentadiene. Exemplary tetrapolymers include ethylene/propylene/1-octene/diene (ENB) and ethylene/propylene/mixed dienes, such as ethylene/propylene/5-ethylidene-2-norbornene/piperylene. In addition, the elastomers made using the process of this invention can include minor amounts, for instance, 0.05 - 0.5 percent by weight, of long chain branch enhancers, such as 2,5-norbornadiene (which is bicyclo[2.2.1]hepta-2,5-diene), diallylbenzene, 1,7-octadiene ($\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$), and 1,9-decadiene ($\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_6\text{CH}=\text{CH}_2$).

At a general minimum, the elastomers made by the process of this invention comprise at least 30, preferably at least 40 and more preferably at least 50 weight percent ethylene; at least 15, preferably at least 20 and more preferably at least 25 weight percent of at least one α -olefin; and if present, preferably at least 0.1 and more preferably at least 0.5 weight percent of at least one conjugated or nonconjugated diene. At a general maximum, the elastomers made by the process of this invention comprise not more than 85, preferably not more than 80 and more preferably not more than 75 weight percent ethylene; not more than 70, preferably not more than 60 and more preferably not more than 55 weight percent of at least one α -olefin; and not more than 20, preferably not more than 15 and more preferably not more than 12 weight percent of at least one of a conjugated or

nonconjugated diene. All weight percentages are based on weight of the elastomer which can be determined using any conventional method.

The polydispersity (molecular weight distribution or Mw/Mn) of the interpolymer elastomers generally ranges from 1.5, preferably from 1.8, and especially from 2.0 to 15, preferably to 10, and especially to 6.

Measurement of the polydispersity index is done according to the following technique: The polymers are analyzed by gel permeation chromatography (GPC) on a Waters 150°C high temperature chromatographic unit equipped with three linear mixed bed columns (Polymer Laboratories (10 micron particle size)), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which about 0.5 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 100 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the equation:

$$M_{\text{polyethylene}} = (a) (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, Mw, is calculated in the usual manner according to the formula:

$$M_w = \sum (w_i)(M_i)$$

where w_i and M_i are the weight fraction and molecular weight respectively of the i^{th} fraction eluting from the GPC column. Generally the Mw of the interpolymer elastomers ranges from 10,000, preferably from 20,000, more preferably from 40,000, and especially from 60,000 to 1,000,000, preferably to 800,000, more preferably to 600,000, and especially to 500,000.

The elastomers made by the process of this invention cover a range of viscosities, depending upon the molecular weight of the elastomer and optional post polymerization rheological modification. In general, the viscosity of elastomers is characterized by Mooney viscosity which is measured according to ASTM D 1646-89, using a shear rheometer at 125°C. The Mooney viscosity for the elastomers generally ranges from a minimum of 1, preferably 5, more preferably 10, and especially 15 to a maximum of 150, preferably 125, more preferably 100, and especially 80.

The density of the elastomers is measured according to ASTM D-792, and these densities range from 0.850 grams/cubic centimeter (g/cm^3), preferably from 0.853 g/cm^3 , and especially from 0.855 g/cm^3 , to 0.895 g/cm^3 , preferably to 0.885 g/cm^3 , and especially to 0.875 g/cm^3 .

Exemplary catalysts used in the process of this invention are metallocene complexes, and these catalysts and methods for their preparation are disclosed in USSN 545,403, filed July 3,

1990 (EP-A-416,815); USSN 702,475, filed May 20, 1991 (EP-A-514,828); as well as US-A-5,470,993; 5,374,696; 5,231,106; 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,321,106; 5,470,993; 5,486,632.

In USSN 720,041, filed June 24, 1991, (EP-A-514,828) certain borane derivatives of the foregoing metallocene complex catalysts are disclosed and a method for their preparation taught and claimed. In US-A-5,453,410, combinations of cationic metallocene complex catalysts with an alumoxane are disclosed as suitable olefin polymerization catalysts.

Preferred for use herein are catalyst compositions comprising:

a1) a metal complex corresponding to the formula: $ZLMX_pX'^q$, that has been or subsequently is rendered catalytically active by combination with an activating cocatalyst or by use of an activating technique,

wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4, bound in an η^5 bonding mode to L;

L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

Z is a divalent moiety bound to both L and M via σ -bonds, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally, also comprising nitrogen, phosphorus, sulfur or oxygen;

X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2; said metal complex being rendered catalytically active by combination with an activating cocatalyst or use of an activating technique; or

a catalyst composition comprising a cationic complex a2) corresponding to the formula $(ZLM^*X^*_{p^*})^+A^-$,

wherein: M^* is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to L;

L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Z, and L further may be substituted with from 1 to 8 substituents independently selected from